

Research Article

Time Effects on Morphology and Bonding Ability in Mercerized Natural Fibers for Composite Reinforcement

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Received 29 March 2011; Accepted 3 May 2011

Academic Editor: Susheel Kalia

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Properties of cellulose-derived fibers are extremely sensitive to surface treatment. Many studies have investigated the effects of varying surface treatment parameters in natural fibers to improve fiber-matrix bonding; however, work is still needed to assist with developing better quality control methods to use these fibers in more load-bearing composites. Kenaf fibers were alkali treated, and the surface and morphology were analyzed to determine how treatment time affected the bonding sites in natural fibers. The mechanical behavior was also characterized, and tensile testing reported a 61% increase in strength and a 25% increase in modulus in fibers treated for 16 hours. The increase in tensile properties was assumed to result from increased intermolecular interaction and increased crystallinity in cellulose, which was supported by XRD. On the other hand, FTIR spectroscopy and XPS showed that the amount of hydroxyl groups needed for fiber-matrix bonding decreased at longer treatment times.

1. Introduction

Many plant-based fibers are known to exhibit high mechanical properties and are thought to have the potential to possibly replace some synthetic composite reinforcement [1–4]. Unlike synthetic fibers, natural fibers are inexpensive, lower in density, yearly renewable, carbon neutral, and are known to pose no health hazard to workers [5, 6]. However, many factors can prevent natural fibers from displaying their full potential due to resin-reinforcement incompatibility and the presence of surface impurities.

Hydrophobic layers found in natural fibers, such as lignin, are not favored for interaction with most hydrophilic resins. Lignin, being mostly hydrophobic, shows poor adhesion between the fibers and the resin resulting in low mechanical properties in biocomposites. Typical structures of the most common components in natural fibers, pectin, cellulose, hemicelluloses, and lignin, are shown in Figures 1, 2, 3, and 4, respectively.

Chemical treatment has been a well-known method employed to clean the surfaces of fibers and remove unwanted

components, such as waxes, pectin, hemicellulose, and lignin. The removal of these materials has been observed to help with improving interfacial bonding with the commonly used industrial resins [7]. In addition, since the cellulose content increases, the fiber tensile properties also improve. However, the success of treatment in cellulose-based fibers depends not only on the type of treatment, but also on treatment parameters, such as time, concentration, and temperature.

Previous studies have revealed how various methods such as silane, alkali, peroxide, and isocyanate treatments affect the properties of natural fibers [8, 9]. Out of these methods, it has been observed that one of the simplest, most economical and effective forms of treatments with least environmental impact, is alkali treatment particularly mercerization using NaOH [10]. Much work has been done with alkali treating natural fibers for use in composites [11, 12]. Temperature-dependent alkali treatment studies have shown how fibrillation is affected with increased treatment temperatures [13]. At higher temperatures, it was discovered that fibrillation and the removal of noncellulose components

Report Documentation Page			Form Approved OMB No. 0704-0188		
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1. REPORT DATE 2011		2. REPORT TYPE		3. DATES COVERED 00-00-2011 to 00-00-2011	
4. TITLE AND SUBTITLE Time Effects On Morphology And Bonding Ability In Mercerized Natural Fibers For Composite Reinforcement				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory, WPAFB 2941 Hobson Way, Materials & Manufacturing Directorate, Dayton, OH, 45433				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES International Journal of Polymer Science Volume 2011 (2011), 9 pages					
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 10	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

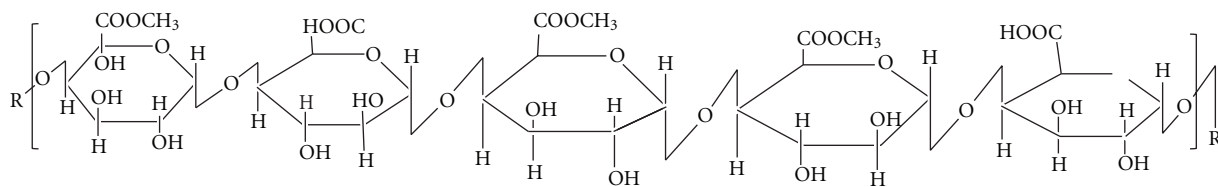


FIGURE 1: Structure of pectin.

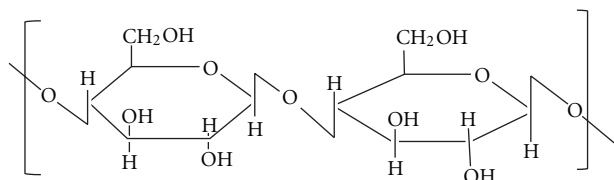


FIGURE 2: Cellulose structure.

occurred at a faster rate [13]. On the other hand, if the treatment temperature is too high, it is possible to deteriorate cellulose, resulting in lower mechanical properties of the fibers.

Literature has also shown the effect of varying alkali concentrations and times during natural fiber mercerization [14]. In one study, jute fibers were treated with multiple alkali solutions at two different times. The authors reported a 79% increase in modulus in jute fibers [15]. Another group of authors investigated how different alkali treatment times and concentrations affected properties of Indian grass fibers [16]. SEM showed that fibers were finer in size after mercerization, which could have been evidence of increased fiber fibrillation. On the other hand, plant-based fibers are fairly difficult to measure due to the inconsistencies with varying fiber diameters.

A 40% increase in tensile and impact properties was reported in alkali-treated Indian grass-reinforced biocomposites. The increase in mechanical properties was believed to be caused from better dispersion of finer fibers, which improved reinforcement ability in the composites. Increased mechanical properties were also believed to result from the presence of increased hydroxyl groups at different treatment times and concentrations. The effects of alkali treatment on the tensile and impact properties of natural fiber-reinforced biocomposites were also studied by Suizu et al. [11]. Suiza et al. alkali treated unidirectional ramie yarns for 2 hours with a 15 wt% NaOH solution. After fabricating the biocomposites using a biodegradable thermoplastic resin, an increase in mechanical properties of ramie-reinforced biocomposites was observed. It was assumed that the increase in impact and tensile properties were caused by enhanced interfacial bonding between the fibers and resin [11].

In another study, curaua fibers were alkali treated for 2 hours with a 10 wt% or 15 wt% NaOH solution and used as reinforcement in a thermoplastic matrix [12]. Although several different composite processing methods were studied, biocomposites that contained alkali-treated curaua fibers showed superior tensile properties compared to untreated

curaua biocomposites. Once again, the increase in tensile properties was assumed to be the result of an increase in interfacial bonding between the fibers and matrix, which was caused from the removal of lignin and other incompatible ingredients [12].

Most time-based studies have generally shown that longer treatment times lead to better mechanical properties and enhanced cellulose exposure [17]. However, fibers can also exhibit lower mechanical properties if treated too long. As previously stated, the mechanical performance and composition of natural fibers can be influenced significantly by alkali treatment parameters. Unfortunately, treatment times in many natural fibers have not been extensively analyzed to determine how the duration of treatment affects the morphology, surface chemistry, and fiber bonding for later use with common resins, such as epoxies and polyesters.

The objective of this study, therefore, is to investigate how treatment times influence the surface changes, morphology, and, hence, bonding ability in natural fibers. All of these factors can severely influence the effectiveness of using natural fibers in composites. For example, if a certain type of fibers has high mechanical properties, but the amount of sites available for bonding is low, treatment would prove to be ineffective. Since the overall mechanical properties of composites are heavily dependent upon fiber-matrix adhesion, providing means to enhance interfacial bonding is crucial.

In the present study, bast kenaf fibers were alkali treated with sodium hydroxide (NaOH) solution, and the fibers were characterized using FTIR spectroscopy and XPS, XRD, SEM, and Instron tensile testing to characterize the structural changes, crystallinity, surface, and tensile properties, respectively. Kenaf plant is considered as a weed and, hence, does not need much care before or during its growth. It is also fairly disease resistant. As a result, kenaf is one of the least expensive natural fibers and, if processed properly, expansion in its use as reinforcement in "green" and other composites is possible. The fibers are extracted from the stem of the plants and are also known as bast fibers. This type of fiber has been used in paper, furniture, and textile applications, and, with treatment, it can also be used as reinforcement in some composite structures.

2. Materials and Methods

2.1. Treatment of Kenaf Fibers. Kenaf fibers (Kenaf Industries of South Texas, Raymondville, TX, USA) were treated using NaOH. The NaOH solution was prepared by dissolving

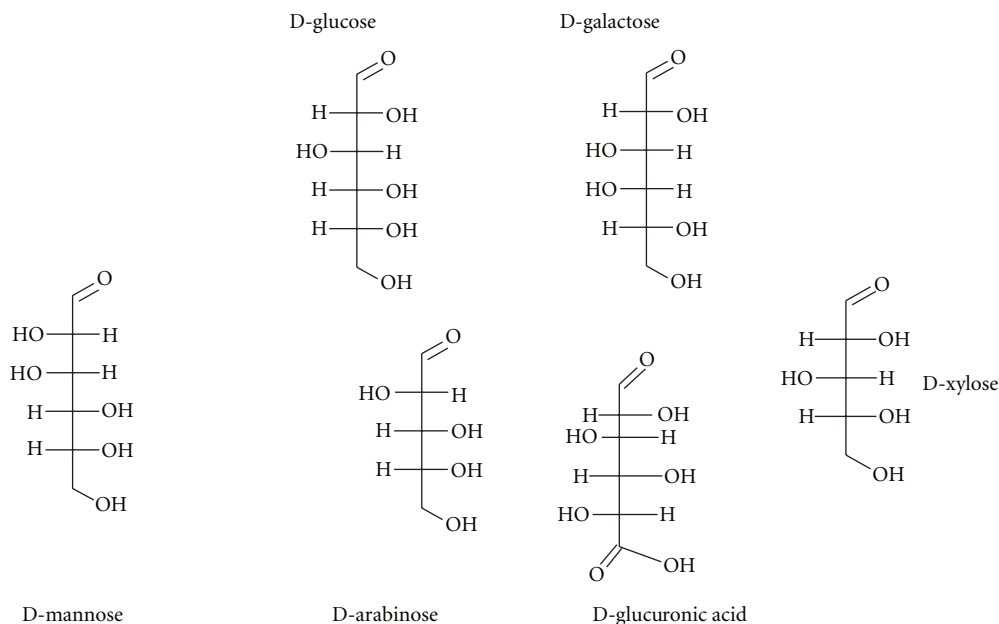


FIGURE 3: Various sugars of hemicelluloses.

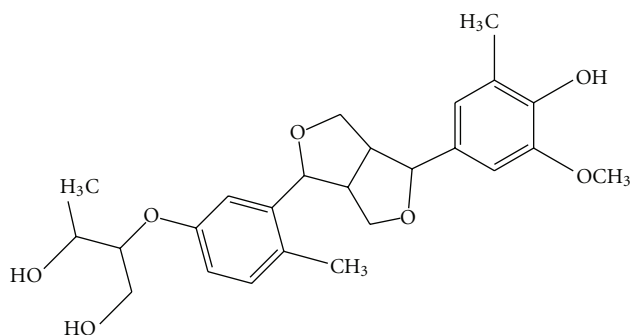


FIGURE 4: Proposed structure of lignin.

NaOH pellets (Fisher Scientific) in deionized water to make up a 7 wt% of NaOH solution. Small bundles of kenaf fibers were cut approximately 44 mm in length and were soaked in alkali solution. The fibers made up 0.35 wt% of the NaOH solution. The fibers were alkali treated for 0.5, 1, 2, 4, 8, 16, and 24 hours at room temperature. After the treatment was complete, the fibers were rinsed thoroughly in distilled water until a neutral pH was obtained. The fibers were later dried in a vacuum oven at 80°C for 24 hours to ensure that all residual moisture was removed. An example of the alkali treatment reaction is shown in Figure 5.

2.2. Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy. The effect of alkali treatment on the surface of kenaf was studied using a Nicolet IR spectrometer in attenuated total reflectance (ATR) mode. This technique was used to study how alkali treatment times affected the surface properties of bast kenaf fibers. Generally, this method is carried out by placing a sample on a small

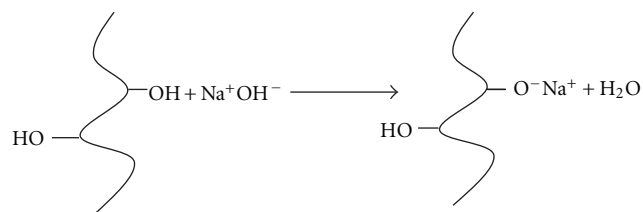


FIGURE 5: Alkali treatment reaction of cellulose-based fibers with NaOH.

crystal of a certain refractive index. The energy from the IR beam protrudes a few micrometers from the crystal and onto the sample surface. The absorbed energy from the surface of the sample is then passed to the IR detector. A diamond crystal was used, and 64 scans with a resolution of 4 cm⁻¹ were collected for each spectrum. Additionally, ATR-FTIR spectroscopy was used to determine the effect of alkali treatment time on the mean hydrogen bond strength (MHBS) in kenaf. The MHBS was calculated by the use of the following equation:

$$\text{MHBS} = \frac{A_{(\text{OH})}}{A_{(\text{CH})}}, \quad (1)$$

where $A_{(\text{OH})}$ denoted the absorption of the hydroxyl stretching vibration in the region located at ~3300 cm⁻¹ wavenumber, and $A_{(\text{CH})}$ corresponded to the absorption activity occurring in alkyl groups at 2980 cm⁻¹ wavenumber [18].

2.3. X-Ray Photoelectron Spectroscopy (XPS). XPS was used to study the elemental compositions on the surfaces of kenaf following alkali treatment. This technique was carried out

using surface science instruments (SSI) M-Probe spectrometer using an incidence angle of 55° where 95% of the signal comes from a depth of $3x$ (inelastic mean free path) $\times \sin(55^\circ)$. The samples were subjected to both low- and high-resolution scans. A survey scan was carried out to determine which elements were present. The peaks of interest were carbon and oxygen whose binding energies appeared in the ~ 290 – 270 and ~ 540 – 520 eV ranges, respectively. With this particular method, changes in the levels of the oxygen to carbon ratio (O:C) was assumed to be an indication of the presence or removal of hemicellulose and lignin. Casa software was used to analyze the peaks of interest. Casa processing software offers analysis techniques for both spectral and imaging data.

2.4. Scanning Electron Microscopy. The surfaces of untreated and alkali-treated kenaf were studied using a Jeol JSM 5800 scanning electron microscope with an accelerating voltage of 15 kV. The fibers were sputtered with Au/Pd for 5 minutes prior to imaging. The samples were sputtered using a Hummer 6.2 sputter coater by Anatech Ltd. to help eliminate charging on the samples during imaging.

2.5. Tensile Testing of Kenaf Fibril Bundles. The mechanical behavior of kenaf fibril bundles was characterized using an Instron Model 5566 materials testing system. Treated and untreated kenaf fibers were placed in a chamber maintained at ASTM conditions of 71°F (21°C) and 65% RH for 72 hours prior to testing. Specimens were prepared by mounting the bundles on paper tabs and securing the tips of the bundles with tape and glue. The kenaf bundles were tested using an effective gauge length of 30 mm. The diameters of the fibril bundles were determined using an optical microscope. A 100N load cell was used, and the fibers were strained at a rate of 4%/min. Bluehill software (version 1.2.) was used to analyze the data. At least 20 specimens were tested for each treatment times.

2.6. X-Ray Diffraction. X-ray diffraction was used to determine the effects of alkali treatment on the morphology of kenaf. XRD was carried out using a Rigaku Ultima diffractometer with a Cu $K\alpha$ detector to determine if there was any effect on the crystallographic order in the fibers at various treatment times following alkali treatment. Samples were scanned at $5^\circ/\text{min}$ across the range of 10 – 80° (2θ) using a step size of 0.2° , a voltage of 20 kV, and a current of 20 mA.

3. Results and Discussion

3.1. Effect of Alkali Treatment on Fiber Surface Functionality. Figure 6 shows the changes in chemical functionality in the ATR-FTIR spectra in untreated and alkali-treated kenaf fibers for all treatment times. It was observed that the absorption peak at $\sim 1730\text{ cm}^{-1}$ wavenumber in as-received kenaf disappeared in as short as 30 minutes following treatment. The removal of this carbonyl peak corresponded to its removal from either carboxylate ($-\text{COOH}$) groups or (COO) ester linkages in pectin [19]. It is assumed that this peak belonged

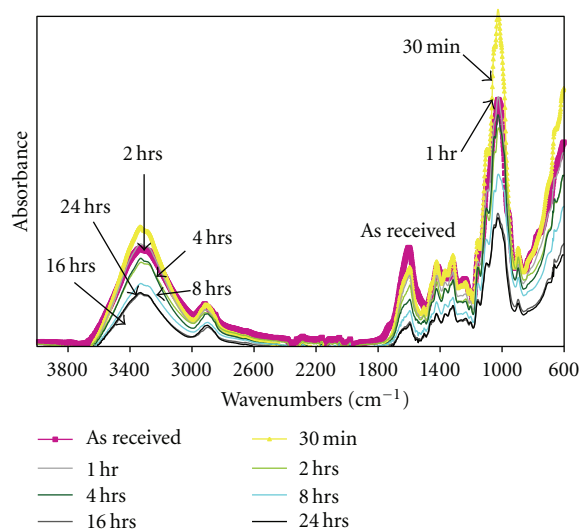


FIGURE 6: Effect of alkali treatment on surface functionality of kenaf fibers.

to carboxylate or ester linkages in pectin, because room temperature treatment using a 7 wt% NaOH solution may have been incapable of removing significant amounts of hemicelluloses in 30 minutes. The absorption peak located at $\sim 1600\text{ cm}^{-1}$ wavenumber appeared to decrease as alkali treatment time increased. This absorption was believed to belong to the $\text{C}=\text{C}$ bonds or aromatic bonds from lignin and was an indication that more lignin was removed as the length of mercerization increased [20].

The intensity in the absorption peaks located at $\sim 1040\text{ cm}^{-1}$ wavenumber was also observed to decrease as treatment time increased. This change was possibly an indication of a decrease in absorption from $\text{C}-\text{OH}$ or $\text{C}-\text{C}$ stretching groups primarily found in hemicelluloses and/or cellulose [19]. The absorption band found at $\sim 3300\text{ cm}^{-1}$ wavenumber was believed to belong to the hydroxyl-stretching vibration in hemicellulose and/or cellulose as well as absorbed moisture.

According to the spectra, the peak for the hydroxyl ($-\text{OH}$) groups at $\sim 3300\text{ cm}^{-1}$ wavenumber was highest in fibers treated for 30 minutes. This was expected due to some of lignin being removed. It was believed that after lignin was removed, the exposure of hydroxyl groups in hemicellulose and cellulose increased. The intensity of the hydroxyl groups eventually decreased with longer alkali treatment times. Results showed that the hydroxyl stretching vibration continued to decrease as the treatment time increased to 16 hours, which was expected due to the increased degradation of hemicellulose. After 16 hours of treatment, very little changes were observed for the $-\text{OH}$ peak. Since cellulose is fairly resistant to alkali solution, the minimum amount of activity taking place during these times was possibly an indication that mostly cellulose was present on the surface.

The mean hydrogen bond strength (MHBS) was calculated for the fibers at all treatment times. Figure 7 shows the effect of alkali treatment time on MHBS. According to the plot in Figure 7, the MHBS was highest for untreated

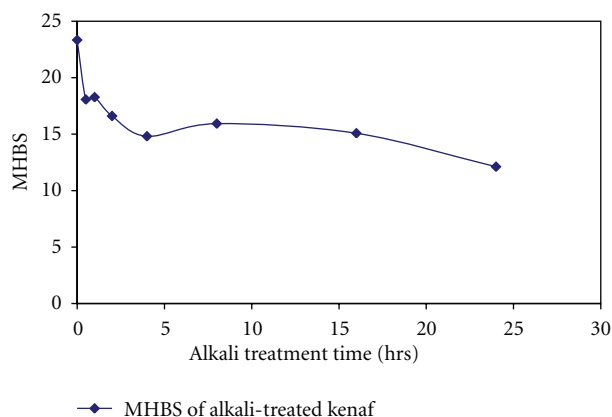


FIGURE 7: Effect of time on MHBS of alkali-treated kenaf fibers.

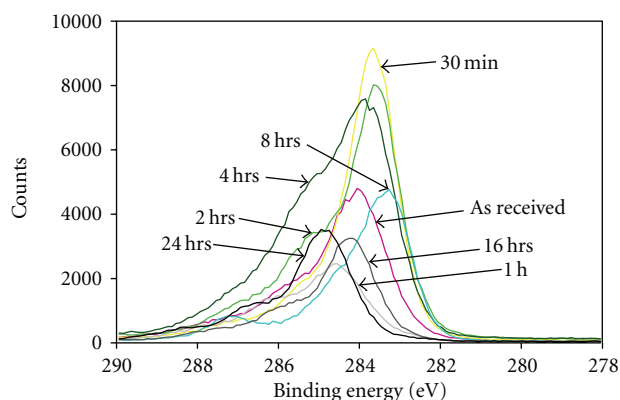


FIGURE 9: Carbon region of XPS spectra in untreated and alkali-treated kenaf fibers.

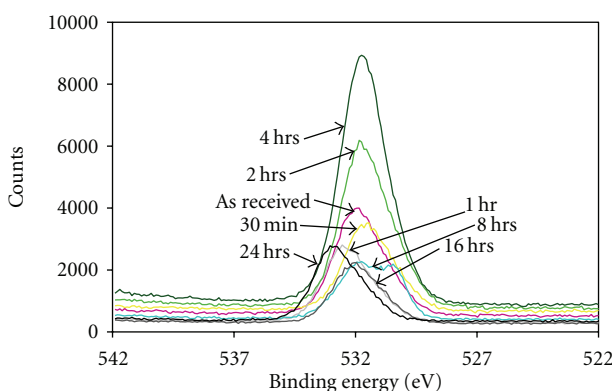


FIGURE 8: Oxygen region of XPS spectra in untreated and treated kenaf fibers.

kenaf. As the treatment time increased, the MHBS strength decreased, with the most significant decrease occurring between 30 minutes and 4 hours. Between 8 and 24 hours, the MHBS continued to gradually decrease. The sharp decrease in MHBS for kenaf alkali treated at shorter treatment times, confirm that the most significant changes taken place are a result of the removal of lignin and hemicellulose. The fact that the MHBS was highest for the untreated fibers was expected. Lignin has been known to form strong hydrogen bonds with hemicellulose, cellulose, and pectin, which was an indication why the MHBS was highest for untreated kenaf [21]. However, as mentioned earlier, the alkali treatment is capable of removing lignin and hemicellulose by disrupting the hydrogen bonding formed with cellulose by swelling the fiber cells [22]. As the hydrogen bonding was disrupted, a decrease in MHBS was observed in kenaf with increased treatment time.

3.2. XPS Surface Analysis of Alkali-Treated Fibers. In the XPS surface analysis scans, oxygen and carbon were the main elements of interest. As discussed, all natural fibers consist of hemicellulose, cellulose, pectin, and lignin. However, the major differences in properties of natural fibers are a result of varying concentrations of these constituents. Hemicellulose and pectin are both polysaccharides, while cellulose is a sugar

molecule as well. As a result, carbon and oxygen primarily make up the structures of these particular fiber layers. In some cases, however, it has been reported that hemicellulose may contain some nitrogen atoms in its structure [23]. Another point to note is that lignin is mostly made of hydrocarbons and is known to be either highly aromatic or highly unsaturated. For this reason, lignin is expected to possess a very low O : C ratio.

The changes in the oxygen and carbon regions associated with these elements are shown in Figures 8 and 9, respectively, for all alkali treatments. According to the data in Figures 8 and 9, the peaks that corresponded to the presence of oxygen and carbon fluctuated considerably in both intensity and broadness. Because of the variance, the peak ratios were studied to gather quantitative information in regards to how the length of treatment affected the surface chemistry of kenaf fibers.

Analysis of the data was carried out by measuring the areas under the curves and calculating the O : C ratios at each treatment time. These data are presented in Table 1. According to the data in Table 1, the as-received fibers contained an O : C ratio of ~ 0.87 . After the first 30 minutes of treatment, the O : C ratio showed a noticeable decrease to 0.49 followed by an increase to almost a 1 : 1 O : C ratio for 1 hour treatment. The low O : C ratio observed at 30 minutes after treatment could be attributed to the removal of pectin and increased exposure of lignin on the fiber surface. Pectin is a complex structure that contains many hydroxyl and carboxyl groups. When NaOH is added to pectin, the sugars were possibly broken down and removed, leading to exposure of lignin. The O : C ratios between 1 and 4 hours were higher than at 30 minutes, but eventually decreased and appeared somewhat constant at 0.79 for treatments between 16 and 24 hours. This constant trend could have signified the increased exposure of cellulose, which is fairly resistant to NaOH treatment.

3.3. Scanning Electron Microscopy of Untreated and Alkali-Treated Kenaf Fibers. The effect of alkali treatment on the surfaces of kenaf fibers is shown as SEM photomicrographs in Figures 10(a) and 10(f). According to Figure 10(a),

TABLE 1: Oxygen to carbon ratio for untreated and alkali-treated kenaf fibers.

	0 hr	0.5 hr	1 hr	2 hrs	4 hrs	8 hrs	16 hrs	24 hrs
Oxygen	2155.9	1749.3	1551.1	1896.2	2321.8	1528.3	1513.1	1598.0
Carbon	2475.0	3550.0	1552.0	2031.0	2393.0	2451.0	1924.0	2035.3
O : C ratio	0.87	0.49	1.00	0.93	0.97	0.62	0.79	0.79

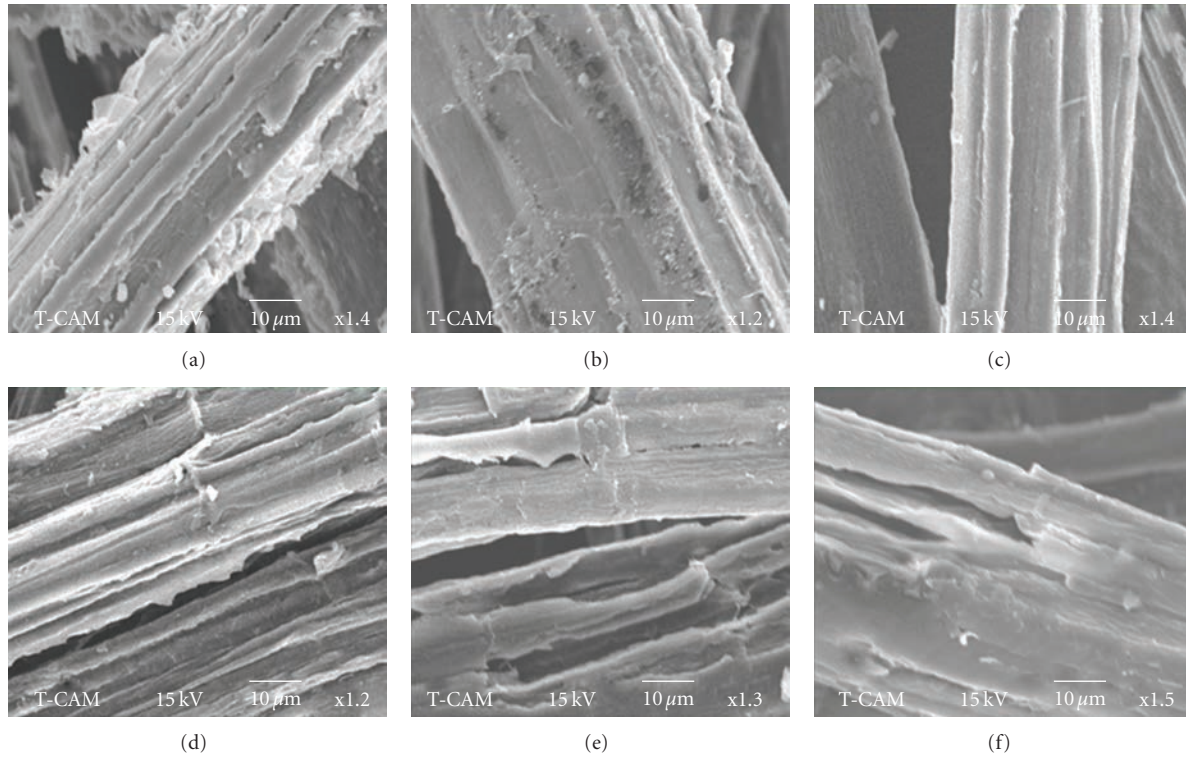


FIGURE 10: SEM of kenaf fibril bundles for (a) untreated fibers and kenaf fibril bundles treated for (b) 30 minutes, (c) 2 hours, (d) 4 hours, (e) 16 hours, and (f) 24 hours.

untreated kenaf contained considerable amounts of unwanted impurities on the kenaf surface. At 30 minutes (Figure 10(b)), it appeared that alkali treatment was successful with removing the surface contaminants. As the treatment time increased beyond 2 hours (Figure 10(c)), an increase in surface roughness was observed. This was believed to be caused from the deterioration of lignin and hemicellulose, the components that essentially bind individual fibrils into bundles to form fibers. The reduction in the amount of fibril bundles (commonly known as fibrillation) was assumed to lead to an increase in exposure of more reactive cellulose groups on the fiber surfaces.

As the treatment time approached 16–24 hours (Figures 10(e) and 10(f)), more evidence of breakage or damage on the fiber surfaces was observed. It is quite possible that some of the fibrils that were sufficiently loosened were lost and the inner surface, which consisted of hemicellulose and lignin and bound cellulose fibrils, was exposed. According to these observations, treating kenaf for longer than 16–24 hours would damage the fibers, and a decrease in mechanical performance would be noticed. On the contrary, what may have appeared as cracks on the kenaf surfaces could have

been evidence of more fiber fibrillation from the removal of more hemicellulose.

3.4. Mechanical Property Evaluation of Alkali-Treated Kenaf Fibers. Figures 11(a) and 11(b) show the effects of alkali treatment times on the tensile stress and moduli, respectively, for kenaf fibers. According to Figure 11(a), the tensile stress increased as the treatment time increased from 195.4 MPa for control to a maximum of 314.9 MPa at 16 hour. When treated for 24 hours, the tensile stress of the fiber bundles decreased to 226.2 MPa. It was confirmed from statistical analysis that the tensile strength was significantly higher after treating kenaf for 8 hours.

The effect of alkali treatment on the Young's modulus of kenaf fibers is shown in Figure 11(b). The modulus for control fibers was 21.1 GPa. However, the modulus fluctuated between 18.1 GPa and 20.9 GPa for treatments of 30 minutes and 4 hours. However, the modulus eventually increased as the treatment times increased beyond 4 hours. The decrease in stiffness observed at 30 minutes may have been caused by the removal of lignin, the rigid component on the fibers. The increased modulus in kenaf fibers treated

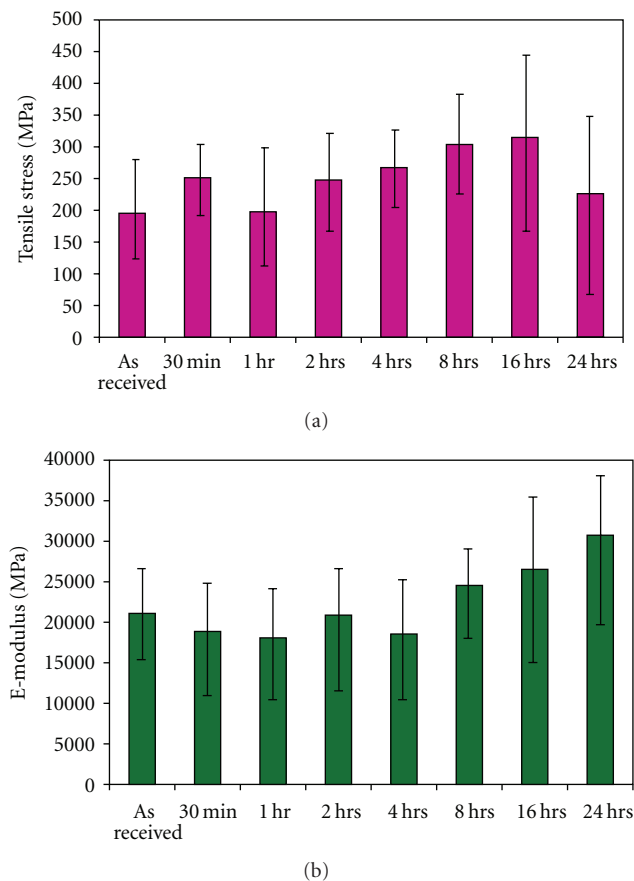


FIGURE 11: Effect of alkali treatment time on (a) tensile stress and (b) Young's moduli in untreated and alkali-treated kenaf fibril bundles.

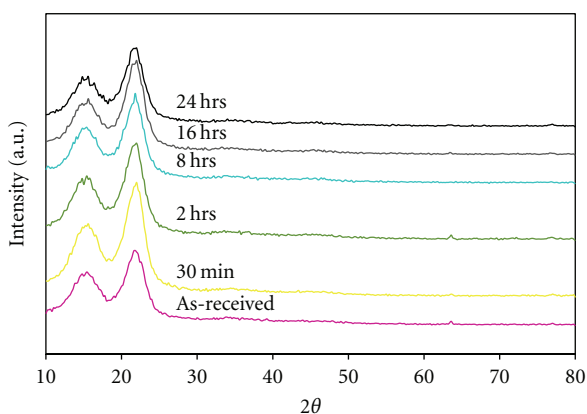


FIGURE 12: Effect of alkali treatment on crystallinity of as-received and alkali-treated kenaf.

beyond 4 hours was believed to be attributed to an increase in cellulose crystallinity.

3.5. Effect of Alkali Treatment Times on Morphology and Cellulose Crystallinity. Cellulose is the only constituent in the fiber that exists in crystalline form since it is the only

TABLE 2: Effect of time on FWHM in kenaf fibers.

Treatment time (hrs)	2θ (degrees)	Average FWHM (degrees)
0	~ 22.0	1.20 ± 0.021
0.5	~ 22.0	1.22 ± 0.082
2	~ 22.0	1.15 ± 0.051
8	~ 22.0	1.06 ± 0.093
16	~ 22.0	1.06 ± 0.15
24	~ 22.0	1.00 ± 0.084

linear and regular molecule in the fiber that is capable of crystallizing. Figure 12 shows the effect of alkali-treatment on the crystallinity of as-received and alkali treated kenaf fibers. Because kenaf fibers were assumed to be more crystalline, XRD was used to confirm the time-based effects of alkali treatment on the crystallinity of cellulose. According to Figure 12, the major peak of interest in the X-ray diffractograms was the crystalline peak for cellulose, located at $\sim 22^\circ 2\theta$. It was determined that the crystal lattice planes were located in the 002 direction. According to the diffraction patterns, the peak for crystalline cellulose did not appear to show significant changes as the treatment time varied. The full width at half maximum (FWHM) was calculated for the peaks belonging to crystalline cellulose to get a better representation of the changes taking place in order as a result of treatment.

Typically, smaller FWHM values observed in fibers represent materials with higher crystalline contents as this means sharper or narrower peaks. Previous work has shown that the FWHM could provide information about the crystallite sizes of cellulose as well [24, 25]. According to Table 2, the FWHM values decreased as the treatment time increased. This suggested that the amount of crystalline content in cellulose increased as treatment time increased and supported evidence of the tensile property improvements in kenaf. Previous work has reported that an increase in crystallinity could be caused by an increase in van der Waals and hydrogen bonding between neighboring molecules as a result of the increased interaction of hydroxyl groups found in cellulose [26]. On the other hand, the increase in crystallinity could have been caused by the removal of the amorphous parts of the fibers from alkali treatment.

4. Conclusions

Effects of alkali treatment times on the surface chemistry, morphology, and bonding were studied in bast kenaf fibers. ATR-FTIR spectroscopy, XPS, and SEM showed that the most significant chemical changes on the surfaces occurred between 30 minutes and 4 hours of treatment; however, fibers treated for 16 hours showed the most significant increase in tensile strength.

SEM photomicrographs illustrated that alkali treatment was successful in removing waxes and unwanted surface impurities. ATR-FTIR spectroscopy showed gradual changes consistent with the removal of hemicellulose and lignin. After 16 hours of alkali treatment, the surface chemistry did not

appear to show any significant changes according to ATR-FTIR spectroscopy and XPS. With higher times, the inner surfaces were being exposed as more materials were being removed. XPS and ATR-FTIR spectroscopy also showed that the amounts of hydroxyl groups on the fiber surfaces decreased as treatment time increased. This suggested that there was a decrease in the number of sites available for hydrogen bonding in kenaf when treated between 8 and 24 hours according to XPS and between 2 and 24 hours according to the MHBS calculations from ATR-FTIR spectroscopy.

Alkali treated-kenaf fibers displayed the highest tensile properties at 16 hours of treatment; however, using this group of fibers in a composite would ultimately result in poor properties. Fiber-resin bonding is the biggest factor that affects mechanical properties in composites. Since it was observed that longer treatment times resulted in fewer surface hydroxyl groups on the kenaf surfaces, the amount of sites needed for fiber-matrix bonding were reduced and would lead to lower mechanical properties in resulting biocomposites.

It was believed that treating bast kenaf fibers for 2–4 hours would work best as reinforcement in composites, because the mechanical properties in fibers were slightly higher, and more hydroxyl groups in cellulose were available to bond with compatible functional groups in resins. To conclude, when treating natural fibers for use as composite reinforcement, it is essential to establish a proper balance among fibers that will yield increased mechanical properties and fibers that will provide optimal bonding.

Acknowledgments

The authors would like to thank NSF Alabama EPSCoR and ACHE for funding as well as Chuck Taylor at Kenaf Industries of South Texas for supplying the kenaf fibers. NSF Alabama EPSCoR Grant, Alabama Commission for Higher Education (ACHE).

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